Radiocarbon in Marine Dissolved organic carbon

Clercq, Martijn le

8 Conclusions

The aim of this project was to quantify the cycling of Dissolved Organic Carbon (DOC) in the oceans on the basis of carbon isotope ratios. DOC ^{14}C activities show the cycling velocity and DOC $\delta^{13}C$ gives insight in the marine or terrestrial origin of DOC.

Initially, it was assumed that both the wet chemical and the UV oxidation method could not be trusted to result in complete oxidation, therefore not yielding reliable results. It appeared that so far only the high temperature catalytic oxidation method could quantitatively oxidize all DOC. Later studies showed that the discrepancies between the different oxidation methods were mainly caused by incorrect blank subtractions and sample storage problems, not so much by oxidation efficiencies.

The construction of a supercritical oxidation for larger samples required for isotope ratio measurement was sucessful. It offers a valuable independent measurement technique to the existing ones, although the required time per sample is high, especially as a new alumina tube has to be installed after every sample. The ceramic reactor itself is a useful spin-off from the oxidation system. It greatly expands the range of fluids that can be used in supercritical reactions. Its main problem is formed by the release of slivers from the wall after cooling. Tests with other types of alumina or continuous heating instead of cooling in between samples might solve that problem.

DOC concentration and carbon isotope ratio profiles have been measured with the supercritical oxidation system. However, the method suffers from a recovery problem which is still unresolved. It is so far unclear whether this incomplete recovery results in isotope fractionation.

The DOC ^{14}C activities confirm the view that the major part of surface DOC and all the deep water DOC is very refractory and is present in the oceans on a time scale of thousands of years. In the North Sea, the presence of anthropogenic ^{14}C in the inorganic carbon fraction hinders the analysis of organic matter dynamics by ^{14}a data.

DOC $\delta^{13}C$ values fluctuate between -20‰ and -22‰. Only relatively inexact information on the relative importance of terrestrial or marine organic matter to the DOC pool can be gained from this $\delta^{13}C$. The large number of mechanisms that can influence DOC $\delta^{13}C$ and the absence of trends with depth, and with ocean or fresh water input limits the use of DOC $\delta^{13}C$ in the analysis of its origin. The loss of samples by contamination with enriched ^{14}C from three different places shows how widespread the problem of careless handling of radioactive matter is. The only way to collect reliable samples onboard a research vessel

where ^{14}C is used, is to flush and poison all bottles elsewhere and limit the handling on board to filling, double packing and storage.

A new ocean model that combines circulation with DOC dynamics has been developed. The DOC dynamics have been validated and calibrated using results from this work in combination with literature data. The concentration and ^{14}C activity of DOC can be reproduced by splitting the DOC into only two types, one labile and one refractory. The decay constant is approximately 0.05 yr^{-1} for the labile and 0.0002 yr^{-1} for the refractory pool. The ratio of particulate and dissolved organic carbon export from the ocean surface to the intermediate 100 to 1000 m depth is roughly 8%. For the export to a depth below 1000 m, the importance of DOC is only 2%.

As the research in DOC has shown that there is no detectable difference between the different oxidation methods, the arguments for choosing the oxidation method are mainly accuracy and analysis time needed per sample. A system that can oxidize several samples simultaneously with UV oxidation or the latest version of the dry combustion system (Fry et al., 1996) seem the most practical options.

With such a system more, internally consistent field data could be gathered. This would also require the use of reference DOC samples because the required precision (1 μM) in deep water DOC concentrations is of the same order as the measurement error with the present calibration methods. Such data would enable more accurate conclusions from a global DOC model as presented in this work.